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Intracuster Reactions of Chlorobenzene/Ammonia Mixed Complexs

by

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INTRACLUSTER REACTIONS OF CHLOROBENZENE/AMMONIA MIXED COMPLEXES

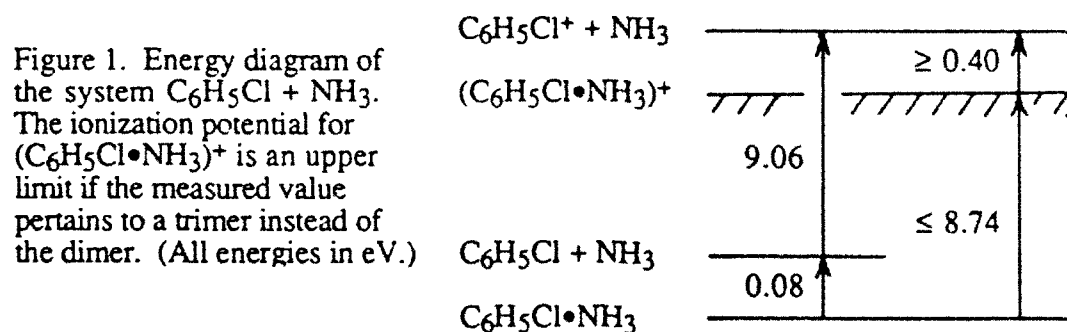
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The spontaneous disintegration of $(\text{C}_6\text{H}_5\text{Cl}\cdot\text{NH}_3)^+$ to form $\text{C}_6\text{H}_5\text{NH}_3^+$ has been extensively studied by two-photon techniques at other laboratories. We examined this process using single-photon interactions, and expanded the work to include larger complexes of $\text{C}_6\text{H}_5\text{Cl} + \text{NH}_3$ and higher energies. The complexes were prepared by jet expansions of 0.50% $\text{C}_6\text{H}_5\text{Cl}$ in NH_3 , using a nozzle 0.010 cm in diameter, the resulting mixtures being analyzed by the method already described¹. A sharp onset of $\text{C}_6\text{H}_5\text{NH}_3^+$ from $\text{C}_6\text{H}_5\text{Cl}\cdot\text{NH}_3$ was found at 8.947 ± 0.003 eV, which, when combined with the known heat of formation of $\text{C}_6\text{H}_5\text{NH}_3^+$, gives a dissociation energy $D(\text{C}_6\text{H}_5\text{Cl}\cdot\text{NH}_3) = \text{ca. } 2 \text{ kcal mol}^{-1}$. Production of $\text{C}_6\text{H}_5\text{NH}_3^+$ from trimers was too weak in the onset region to permit measurement. The ion $\text{C}_6\text{H}_5\text{NH}_2^+$ was also observed, with onsets of 8.849 ± 0.009 and 8.255 ± 0.029 eV from $\text{C}_6\text{H}_5\text{Cl}\cdot\text{NH}_3$ and $\text{C}_6\text{H}_5\text{Cl}(\text{NH}_3)_2$ respectively, clearly below the onset for $\text{C}_6\text{H}_5\text{NH}_3^+$, but far above the thermochemical thresholds near 7.6 eV. For the "parent ions" $(\text{C}_6\text{H}_5\text{Cl}\cdot\text{NH}_3)^+$, $\text{C}_6\text{H}_5\text{Cl}(\text{NH}_3)_2^+$, and $\text{C}_6\text{H}_5\text{Cl}(\text{NH}_3)_3^+$ onsets were found at 8.74 ± 0.02 , 8.652 ± 0.013 , and 8.555 ± 0.012 eV. However, product resolution experiments indicate that in the onset region $(\text{C}_6\text{H}_5\text{Cl}\cdot\text{NH}_3)^+$ is apparently produced entirely from trimers. This value of the dimer ion onset therefore implies that $D[(\text{C}_6\text{H}_5\text{Cl}\cdot\text{NH}_3)^+] \geq \text{ca. } 9 \text{ kcal mol}^{-1}$ (Fig. 1). On the other hand, $\text{C}_6\text{H}_5\text{NH}_3^+$ is produced from $\text{C}_6\text{H}_5\text{Cl}\cdot\text{NH}_3$ at energies > 11.5 eV, a process not yet understood.



¹J. R. Grover, W. J. Herron, M. T. Coolbaugh, W. R. Peifer and J. F. Garvey, *J. Phys. Chem.* **95**, 6473-6481 (1991).

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